

ARNOLD
WHITE &
DURKEE

A PROFESSIONAL CORPORATION
ATTORNEYS AT LAW

Austin
Chicago
Houston
Menlo Park
Minneapolis
Washington

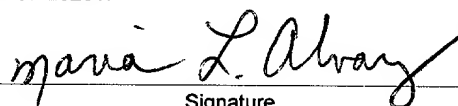
750 Bering Drive
Houston, Texas 77057-2190

Telephone 713.787.1400
Facsimile 713.787.1440

Craig M. Lundberg
Direct Line 713.787.1410

May 26, 1999

FILE: SOLU113

| |
|---|
| EXPRESS MAIL MAILING LABEL |
| NUMBER EL291391777US |
| DATE OF DEPOSIT <u>5-26-99</u> |
| I hereby certify that this paper or fee is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to: Assistant Commissioner for Patents, Washington D.C. 20231. |
|  Signature |

BOX PATENT APPLICATION

Assistant Commissioner for Patents
Washington, DC 20231

RE: *U.S. Patent Application Entitled: "Process for Nitrous Oxide Purification"; J.P. Oppenheim et al.; (14-54(8992))*

Sir:

Transmitted herewith for filing is a 13-page patent specification including 30 claims and an abstract. Also included are Figures 1-6 on 6 sheets. The specification and drawings constitute the application of J.P. Oppenheim, Patrick Notte, Alexander Noskov, Barry Bowman, Ramoorthy Chandrasekhar and Greg Croce for the captioned application.

Please note that this application is filed without an inventors' Declaration and Assignment, a Declaration Claiming Small Entity Status, a Power of Attorney, and filing fees. Pursuant to 37 C.F.R. § 1.53(b) and (d), the Applicant requests the Patent and Trademark Office to accept this application and accord a serial number and filing date as of the date this application is deposited with the U.S. Postal Service for Express Mail. Further, the Applicant requests that the NOTICE OF MISSING PARTS-FILING DATE GRANTED pursuant to 37 C.F.R. § 1.53(d) be sent to the undersigned Applicant's representative.

ARNOLD WHITE & DURKEE

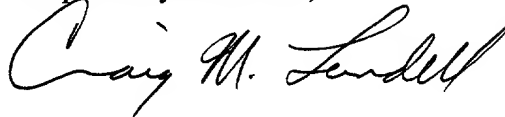
Assistant Commissioner for Patents

May 26, 1999

Page 2

Please date stamp and return the enclosed postcard to evidence receipt of this application.

Respectfully submitted,



Craig M. Lundell

Reg. No. 30,284

CML:scl

Enclosures

cc: John P. Foryt (w/encl.)
Judy Hardy (w/encl.)

659392/20250

PATENT
SOLU:113
14-54(8992)

APPLICATION FOR UNITED STATES LETTERS PATENT

for

PROCESS FOR NITROUS OXIDE PURIFICATION

by

J. P. OPPENHEIM, PATRICK NOTTE, ALEXANDER NOSKOV,
BARRY BOWMAN, RAMOORTHY CHANDRASEKHAR AND
GREG CROCE

| EXPRESS MAIL MAILING LABEL | |
|---|-----------------------|
| NUMBER | <u>EL 291391777US</u> |
| DATE OF DEPOSIT | <u>5-26-99</u> |
| I hereby certify that this paper or fee is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to: Assistant Commissioner for Patents, Washington D.C. 20231. | |
| <u>Maria L. Alvarez</u> | |
| Signature | |

1

2 **FIELD OF THE INVENTION**

3 The present invention relates to a process for purifying a nitrous oxide gas
4 by removal of various impurities.

5

6 **BACKGROUND OF THE INVENTION**

7 A number of processes for purification of off-gases and exhaust gases
8 produced from various thermal power plants are known in the art. Such gases contain
9 undesirable components, such as NOx (nitrogen oxides including NO, N₂O₃, NO₂, N₂O₄,
10 N₂O₅, etc.), sulfur oxides, and the like. These processes are based either on absorption of
11 such impurities by liquid absorbents, or on their conversion (reduction) into harmless
12 compounds (e.g., water vapor and nitrogen in the case of NOx reduction). The most
13 widely employed processes for reduction of NOx use ammonia and selective catalytic
14 reduction (SCR). The SCR processes make it possible to carry out the reduction of NOx
15 to elemental nitrogen and water vapor in the presence of oxygen contained in the off-
16 gases. See U. S. Patents Nos. 5,401,479; 4,859,439; 4,855,115; 4,789,533; 4,438,082;
17 4,720,476; 4,695,438; 4,732,743; 4,975,256; 4,521,388; 5,401,478; and 5,753,582, the
18 entire subject matter of which is incorporated herein by reference. After off-gases are
19 cleaned of minor impurities by conventional processes/equipment, they are vented to the
20 atmosphere.

21 Moreover, there are also known processes for purifying various commercial grade
22 gases, such as inert gases. For example, U. S. Patent No. 4,579,723, the entire subject
23 matter of which is incorporated by reference, utilizes a multi-step catalytic process to
24 remove CO, CO₂, H₂, H₂O, and O₂ from an argon gas.

25 Various processes have been utilized for removing O₂ from very pure nitrous
26 oxide gas produced from stand alone commercial processes for subsequent use in
27 semiconductor manufacturing. In Japanese Kokai No. 06016402, oxygen is removed
28 from commercially produced nitrous oxide using a manganese oxide catalyst. However,
29 oxygen is removed by using oxygen present in the gas to oxidize the catalyst from a

1 lower to a higher manganese oxide, which does not involve catalysis of reactions
2 involving oxygen containing gases to form easily removed products.

3 Heretofore, removal of impurities from nitrous oxide off-gases has not been
4 contemplated. Releasing nitrous oxide off-gases into the environment is a source of
5 pollution and a waste of nitrous oxide that, if economically and feasibly separated from
6 such off-gases to provide a commercial grade nitrous oxide source, could lead to its use in
7 various processes, such as for use in conversion of benzene to phenol by hydroxylation.
8 See U. S. Patents Nos. 4,982,013; 5,001,280; 5,055,623; 5,110,995; 5,672,777; 5,756,861
9 and 5,808,167, the entire subject matter of which is incorporated herein by reference.
10 Accordingly, there is a need in the chemical industry for a process that purifies nitrous
11 oxide off-gases and at the same time commercially and economically produces nitrous
12 oxide suitable for various commercial applications.

13 14 **SUMMARY OF THE INVENTION**

15 The present invention relates to a method for purification of a nitrous oxide gas by
16 feeding the nitrous oxide gas and reducing agent or precursor thereof into a de-oxidation
17 reactor, and performing de-oxidation by reacting the reducing agent or precursor thereof
18 with oxygen using a catalyst to form an inert, in order to deplete the oxygen in the nitrous
19 oxide gas, while limiting the amount of nitrous oxide removed from the nitrous oxide gas.

20 Additionally, the present invention concerns a method for purification of a nitrous
21 oxide gas by feeding the nitrous oxide gas and ammonia or a precursor thereof into a
22 reactor system, performing selective catalytic reduction by reacting the ammonia or
23 precursor thereof with NOx in the nitrous oxide gas using a selective catalytic reduction
24 catalyst, feeding hydrogen or a precursor thereof into the reactor system and performing
25 de-oxidation by reacting the hydrogen or a precursor thereof with oxygen in the nitrous
26 oxide gas using a de-oxidation catalyst.

27 28 **BRIEF DESCRIPTION OF THE DRAWINGS**

29 The present invention will be more clearly understood by reference to the
30 following description of exemplary embodiments thereof in conjunction with the attached

1 drawings, which represent data obtained as a result of an embodiment of a process
2 according to the invention as set forth in EXAMPLES I and II.

4 DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

5 In accordance with the present invention, a nitrous oxide off-gas is purified
6 utilizing catalytic processes to provide an economical source of nitrous oxide suitable for
7 various commercial applications. Moreover, the process of the present invention
8 selectively purifies nitrous oxide off-gas while maintaining the amount of nitrous oxide in
9 the off-gas by selectively reacting out selected impurities in the off-gas. Such a purified
10 nitrous oxide off-gas may be utilized in one-step hydroxylation of benzene to phenol, as
11 set forth in U. S. Patents Nos. 4,982,013; 5,001,280; 5,055,623; 5,110,995; 5,672,777;
12 5,756,861 and 5,808,167, the entire subject matter of which is incorporated herein by
13 reference.

14 In one embodiment of the present invention, nitrous oxide off-gas is passed
15 through an SCR reactor in the presence of ammonia or a precursor thereof to remove
16 (e.g., by reacting) NO_x while at the same time not reducing the amount of nitrous oxide
17 in the off-gas. The reactor comprises at least one catalyst bed and may be of any suitable
18 configuration such as fixed bed reactor, (e.g., metal, parallel plate, ceramic honeycomb,
19 tubular, or a lateral flow reactor). Preferably, the reactor is a lateral flow reactor. A
20 lateral flow reactor allows a pellet type of catalyst to be employed in a fixed bed
21 providing a higher contact efficiency at a lower pressure drop than a honeycomb catalyst
22 in the same service. Intimate mixing between the ammonia vapor and process gas is
23 accomplished with the use of perforated plates.

24 The catalyst may comprise any known NO_x abatement SCR catalyst, such as
25 those based on transition metals, e.g., Ti, V, W, Mo, Mn, Cu, Fe, Cr, Co, Ni, Zn, Sn, etc.
26 The metal may be in the form of an oxide and may be integrated with or placed on a
27 conventional carrier, such as silica and/or alumina. Preferably, an oxide of Ti-V catalyst
28 is used.

29 The catalyst pellets may be formed into any shape, such as cylinders, spheres,
30 discs, rings, etc., or in the form of a honeycomb block and utilized under conventional

1 SCR conditions. These conditions are dictated by the space velocity of the catalyst, its
2 operating temperature, and the NOx loading.

3 For example, ammonia or a precursor thereof is mixed with the nitrous oxide off-
4 gas containing NOx at a molar ratio with respect to the NOx from 0.1 to 2.0, preferably
5 0.5 to 1.5, and more preferably from 0.8 to 1.2. The mixture may be at a temperature
6 from 100°C to 600°C, preferably from 120°C to 400°C, and more preferably from
7 150°C to 300°C. For adipic acid off-gas service where nitrous oxide is to be preserved,
8 a low temperature range between 150 to 350°C is preferable. Space velocities (amount
9 of gas in cubic meters that passes in one hour through one cubic meter of the catalyst
10 (apparent volume of the catalyst bed) stated with the dimension reciprocal hour) in the
11 range from 300 to 100,000 h⁻¹ may be utilized. The process may be conducted under any
12 pressure. However suitable pressures range from about 1 to about 10 atmospheres.

13 The ammonia or precursor thereof reacts with the NOx to form N₂ and H₂O. The
14 nitrous oxide exiting the reactor comprises less than 200 ppm of NOx, preferably less
15 than 40 ppm, and more preferably less than 10 ppm.

16 Prior to entering the reactor, ammonia and a carrier gas are mixed together. The
17 carrier gas may contain any inert gas that does not significantly deactivate the catalyst.
18 For example, the carrier gas may contain steam, hydrogen, argon, etc., or mixtures
19 thereof. Preferably the carrier gas contains steam.

20 In another embodiment of the present invention, nitrous oxide off-gas is passed
21 through at least one reactor in the presence of a reducing agent or precursor thereof and a
22 catalyst to remove oxygen and other impurities, such as organics (e.g., CO, etc.) without
23 reducing the amount of nitrous oxide present in the off-gas. The reactor comprises at
24 least one catalyst bed and may be of any suitable configuration such as a fixed bed, a
25 tubular reactor, or a lateral flow reactor. Preferably, the reactor is a fixed bed reactor.

26 The catalyst may comprise any known oxidation catalyst, such as those based on a
27 noble metal or combination of noble metals (e.g., platinum or palladium, etc.). The
28 catalyst may be integrated with or placed on a conventional carrier, such as silica and/or
29 alumina. Preferably, the catalyst is a palladium metal with an alumina support.

1 The catalyst may be formed into any shape, such as cylinders, spheres, discs,
2 rings, etc., or in the form of a honeycomb block. Preferably, the catalyst is in the form of
3 a honeycomb block.

4 In this embodiment of the present invention, stoichiometric amounts of a reducing
5 agent or precursor thereof is mixed with the nitrous oxide off-gas containing oxygen.
6 The mixture may be at a temperature from 0°C to 600°C, preferably from 5°C to
7 300°C, and more preferably from 10°C to 200°C. Space velocities (amount of gas in
8 cubic meters that passes in one hour through one cubic meter of the catalyst (apparent
9 volume of the catalyst bed) stated with the dimension reciprocal hour) in the range from
10 300 to 100,000 h⁻¹ may be utilized. The process may be conducted under any pressure.
11 However suitable pressures range from about 1 to about 10 atmospheres.

12 The reducing agent or precursor thereof may be mixed with the nitrous oxide off-
13 gas prior to entering the reactor, or in the reactor itself. This may be accomplished using
14 conventional means, such as an inline mixer. Suitable reducing agents include agents that
15 selectively react with oxygen in the nitrous oxide off-gas without depleting the nitrous
16 oxide in the off-gas. For example, the reducing agent may be hydrogen, which
17 selectively reacts (using an appropriate catalyst as described herein) with oxygen present
18 in the off-gas to produce water. In an embodiment of the present invention, it has been
19 discovered that the hydrogen unexpectedly does not deplete the nitrous oxide in the off-
20 gas (hydrogen would have been expected to also react with nitrous oxide to form nitrogen
21 and water. Another suitable reducing agent is, for example, carbon monoxide, which
22 selectively reacts with oxygen to form carbon dioxide without depleting the nitrous oxide
23 present in the off-gas. The reducing gas may contain a mixture of gases, such as
24 hydrogen and carbon monoxide. Preferably, the reducing gas is a hydrogen containing
25 gas. The hydrogen may be provided in any form, including any hydrogen containing gas
26 such as hydrogen plant offgas, offgas from a dehydrogenation process (e.g. ethylbenzene
27 to styrene), etc. Preferably, the hydrogen is provided in the form of pure hydrogen.

28 In another embodiment of the present invention, the nitrous oxide off-gas is
29 passed through an SCR reactor to remove NOx utilizing the NOx abatement process of
30 the present invention and subsequently the nitrous oxide off-gas is passed through a de-

oxidation reactor to remove oxygen and other impurities using the de-oxidation process of the present invention. Alternatively, the de-oxidation process may precede the NOx abatement process. Moreover, such processes may be conducted multiple times and in any order. The NOx abatement and de-oxidation processes may be conducted in a single reactor having multiple catalyst beds or in a single reactor having multiple chambers. Additionally, each of the NOx abatement and de-oxidation processes may be conducted utilizing multiple reactors. Preferably, NOx abatement precedes de-oxidation.

The recovery of nitrous oxide from the nitrous oxide off-gas utilizing the present purification system comprises greater than 50%, preferably greater than 70%, and more preferably greater than 95%.

EXAMPLES

Processes of the present invention are further defined by reference to the following illustrative examples.

EXAMPLE I

A process for purification of a nitrous oxide gas of the present invention is performed as follows:

A 0.2% w/w Pd on alumina catalyst in the form of beads from Johnson-Matthey is exposed to a gas stream of 60 cc/min composed of 2.4 cc/min of oxygen, 36 cc/min of nitrous oxide, and 6 cc/min of helium at 150°C in a quartz reactor. Contact time is 4.6 seconds. Part of the helium gas is gradually replaced by pure hydrogen. Reaction is followed up by analysis of the reactor effluent by mass spectrometry (amu 32 for oxygen, amu 28, 30 and 44 for nitrous oxide, amu 2 for hydrogen, amu 18 for water). Complete reaction of hydrogen is observed in all the tested cases. Figures 1 and 2 illustrate the selective reaction of oxygen with hydrogen, and not with nitrous oxide, respectively. Figure 1 shows the oxygen destruction as a function of the hydrogen flow. Figure 2 demonstrates the percent nitrous oxide destruction as a function of the hydrogen flow. Figure 3 represents the oxygen destruction selectivity as a function of the hydrogen flow.

EXAMPLE II

The same experiment is conducted at 25°C with a contact time of 0.7 sec with the same gas stream composition and velocities. Figures 4 and 5 demonstrate the performance achieved in this set of conditions. Figure 4 shows the oxygen destruction as a function of the hydrogen flow. Figure 5 illustrates the percent nitrous oxide destruction as a function of the hydrogen flow. Figure 6 demonstrates the oxygen destruction selectivity as a function of the hydrogen flow.

EXAMPLE III

The same experiment is conducted at 25°C with a contact time of 0.7 sec with the same gas stream composition and velocity but hydrogen is partially replaced by CO (i.e., up to 50 vol.% CO). Results in terms of oxygen destruction and selectivities are the same as those provided by pure hydrogen.

EXAMPLE IV

A process for purification of a nitrous oxide gas of the present invention is performed as follows:

A commercial SCR catalyst, Grade S-096 supplied by CRI Catalyst Company, Inc., is exposed to an adipic offgas stream of 15 slpm containing .3% NO_x, 8.0% O₂, 26.5% N₂O, .1% CO, .2% organic impurities (on a Carbon basis), and the balance inerts at an inlet temperature of 247°C in an isothermal pipe reactor heated by a sandbath. Space velocity is 15,000 reciprocal hours. The ammonia is fed stoichiometrically to the NO_x levels which are measured with an online NO_x analyzer. The outlet composition is as follows: .044% NO_x, 7.3% O₂, 26.5% N₂O, .2% CO, .008% organic impurities (on a Carbon basis), and the balance inerts.

1 **WHAT IS CLAIMED IS:**

- 2
- 3 1. A method for purification of a nitrous oxide gas comprising;
- 4 feeding said nitrous oxide gas and reducing agent into a de-oxidation reactor;
- 5 performing de-oxidation by reacting said reducing agent with oxygen using a de-
- 6 oxidation catalyst to form an inert, in order to deplete said oxygen in said nitrous oxide
- 7 gas, while limiting the amount of nitrous oxide removed from said nitrous oxide gas.
- 8
- 9 2. A method according to Claim 1, wherein said reducing agent comprises a
- 10 hydrogen containing gas, a carbon monoxide containing gas or an ammonia containing
- 11 gas.
- 12
- 13 3. A method according to Claim 1, wherein said reducing agent is a hydrogen
- 14 containing gas.
- 15
- 16 4. A method according to Claim 1, wherein said inert comprises water, carbon
- 17 dioxide or nitrogen.
- 18
- 19 5. A method according to Claim 1, wherein said inert is water.
- 20
- 21 6. A method according to Claim 1, wherein said nitrous oxide gas comprises NO_x,
- 22 nitrogen, carbon monoxide, carbon dioxide or organic compounds.
- 23
- 24 7. A method according to Claim 6, wherein said NO_x is removed from said nitrous
- 25 oxide gas by selective catalytic reduction using ammonia or a precursor thereof and a
- 26 selective catalytic reduction catalyst.
- 27
- 28 8. A method according to Claim 6, wherein said carbon monoxide and organic
- 29 compounds are removed from said nitrous oxide gas during said de-oxidation.
- 30

- 1 9. A method according to Claim 1, wherein said nitrous oxide gas comprises adipic
2 acid off-gas.
3
- 4 10. A method according to Claim 9, wherein said off-gas comprises between 1000
5 ppmv and 10 vol. % oxygen, and between 100 ppmv and 1% NOx.
6
- 7 11. A method according to Claim 1, wherein up to 99 vol. % of oxygen is removed
8 from said nitrous oxide gas.
9
- 10 12. A method according to Claim 1, wherein said de-oxidation catalyst comprises
11 palladium, platinum, or mixtures thereof.
12
- 13 13. A method according to Claim 7, wherein said selective catalytic reduction catalyst
14 comprises oxides of vanadium, titanium, or mixtures thereof.
15
- 16 14. A method according to Claim 1, wherein said de-oxidation step is performed with
17 more than one reactor.
18
- 19 15. A method according to Claim 7, wherein said selective catalytic reduction is
20 performed in a selective catalytic reduction reactor separate from said de-oxidation
21 reactor.
22
- 23 16. A method according to Claim 15, wherein said selective catalytic reduction
24 reactor is a lateral flow reactor.
25
- 26 17. A method according to Claim 7, wherein steam is used as a carrier gas for said
27 nitrous oxide gas during said selective catalytic reduction.
28

- 1 18. A method according to Claim 7, wherein prior to and subsequent to said selective
2 catalytic reduction, an oxygen containing gas is passed over said selective catalytic
3 reduction catalyst.
4
- 5 19. A method for purification of a nitrous oxide gas comprising;
6 feeding said nitrous oxide gas and ammonia or a precursor thereof into a reactor
7 system;
8 performing selective catalytic reduction by reacting said ammonia or precursor
9 thereof with NO_x in said nitrous oxide gas using a selective catalytic reduction catalyst;
10 feeding a reducing agent into said reactor system;
11 performing de-oxidation by reacting said reducing agent with oxygen in said
12 nitrous oxide gas using a de-oxidation catalyst.
13
- 14 20. A method according to Claim 19, wherein nitrous oxide gas comprises NO_x,
15 nitrogen, carbon monoxide, carbon dioxide or organic compounds.
16
- 17 21. A method according to Claim 19, wherein said reactor system comprises more
18 than one reactor.
19
- 20 22. A method according to Claim 19, wherein said de-oxidation catalyst comprises
21 palladium, platinum or mixtures thereof.
22
- 23 23. A method according to Claim 19, wherein said selective catalytic reduction
24 catalyst comprises oxides of vanadium, titanium, or mixture thereof.
25
- 26 24. A method according to Claim 19, wherein said selective catalytic reduction
27 reactor is a lateral flow reactor.
28
- 29 25. A method according to Claim 19, wherein steam is used as a carrier gas for said
30 nitrous oxide gas during said selective catalytic reduction.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26

26. A method according to Claim 19, wherein prior to and subsequent to said selective catalytic reduction, an oxygen containing gas is passed over said selective catalytic reduction catalyst.

27. A method according to Claim 19, wherein recovery of nitrous oxide from said nitrous oxide gas utilizing said reactor system comprises greater than 95%.

28. A method for purification of a nitrous oxide gas comprising;
feeding said nitrous oxide gas and ammonia or a precursor thereof into a reactor system;
performing selective catalytic reduction by reacting said ammonia or precursor thereof with NO_x in said nitrous oxide gas using a selective catalytic reduction catalyst; while limiting the amount of nitrous oxide removed from said nitrous oxide gas.

29. A method according to Claim 28, wherein nitrous oxide gas comprises NO_x, nitrogen, carbon monoxide, carbon dioxide or organic compounds.

30. A method according to Claim 28, wherein said organic compounds are selectively removed from said nitrous oxide gas stream by said selective catalytic reduction.

ABSTRACT

A method for purification of a nitrous oxide gas by feeding the nitrous oxide gas and a reducing agent into a de-oxidation reactor, performing de-oxidation by reacting the reducing agent with oxygen using a catalyst in order to deplete the oxygen in the nitrous oxide gas, while limiting the amount of nitrous oxide removed from the nitrous oxide gas.

Figure 1

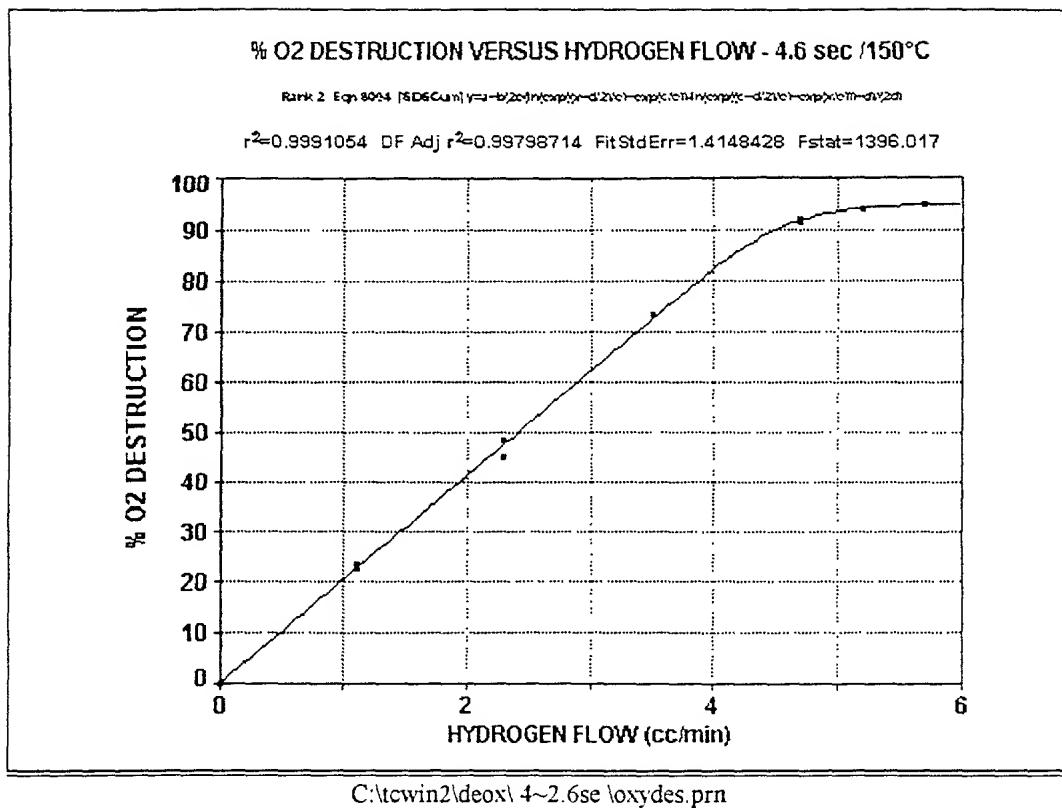


Figure 2

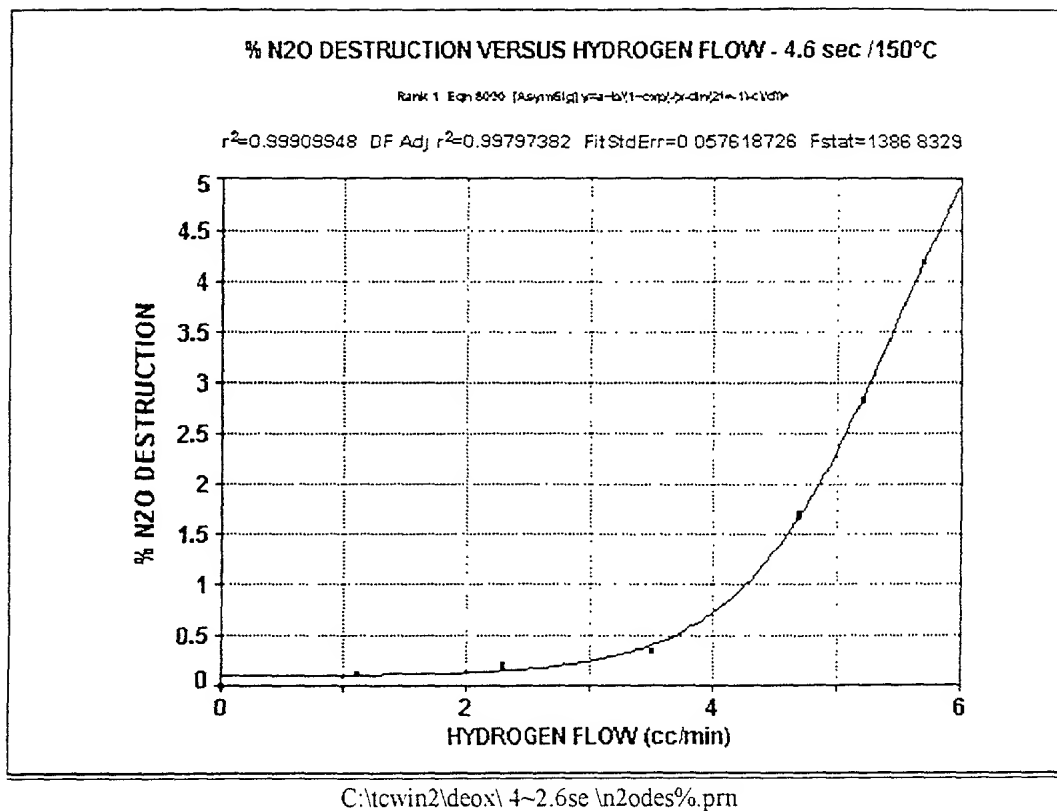
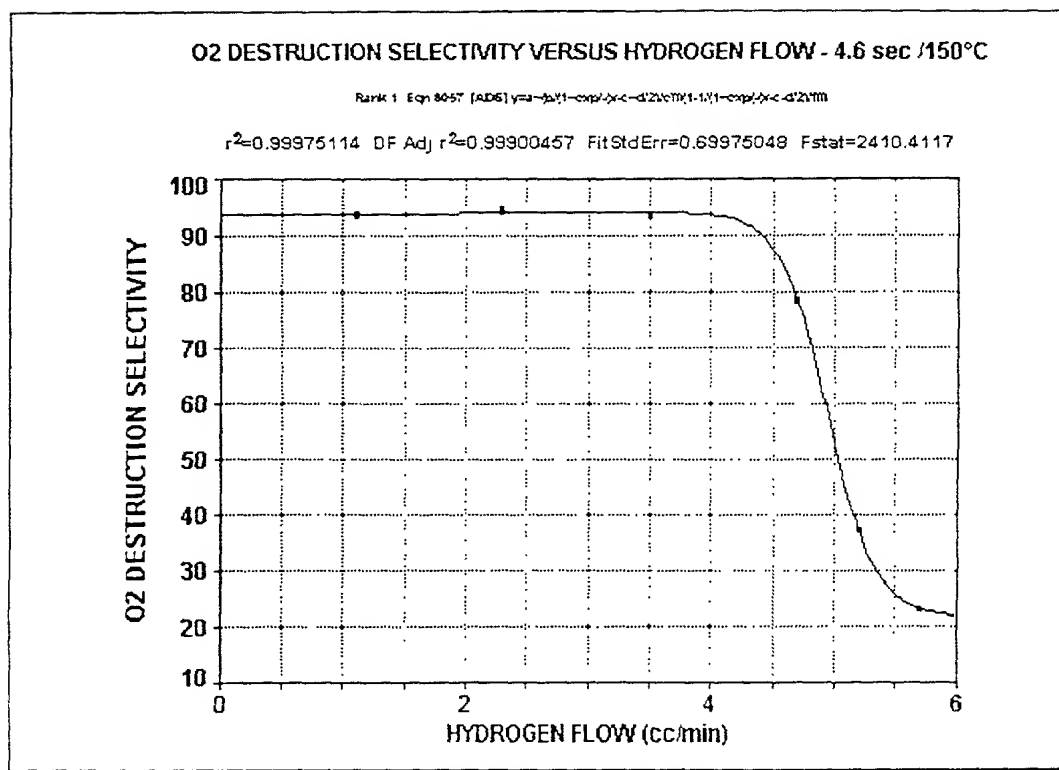


Figure 3



C:\tcwin2\deox\ 4~2.6se \oxysel.prn

Figure 4

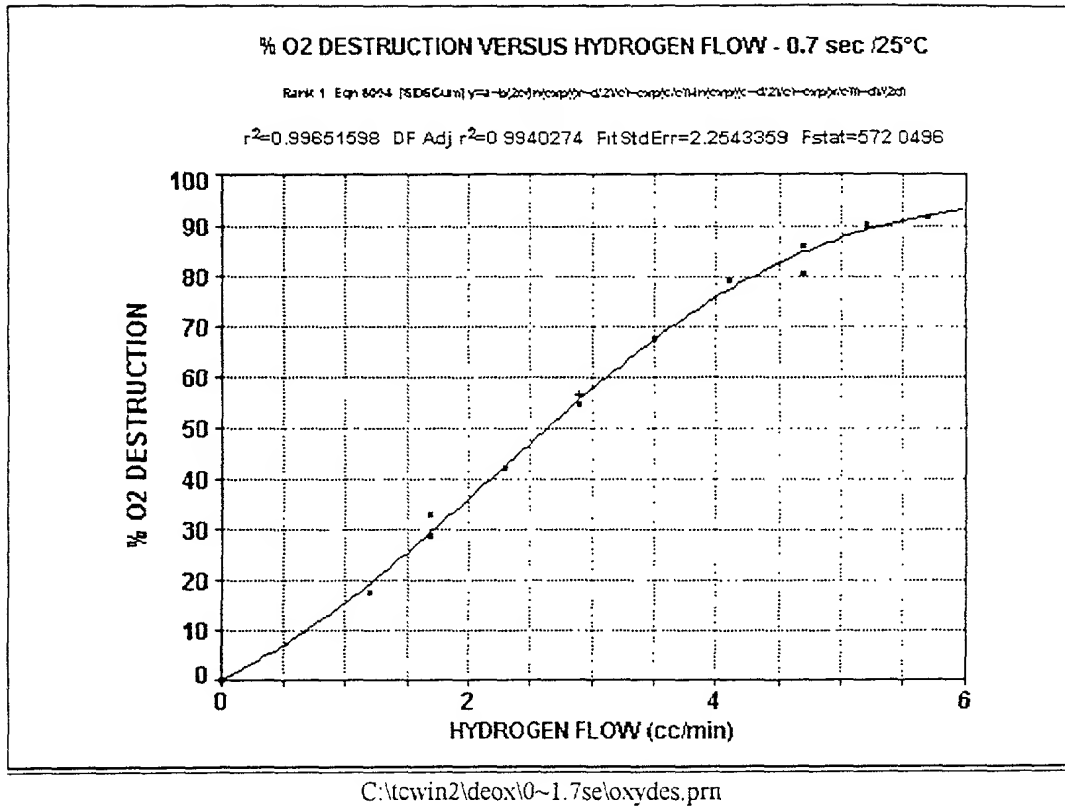


Figure 5

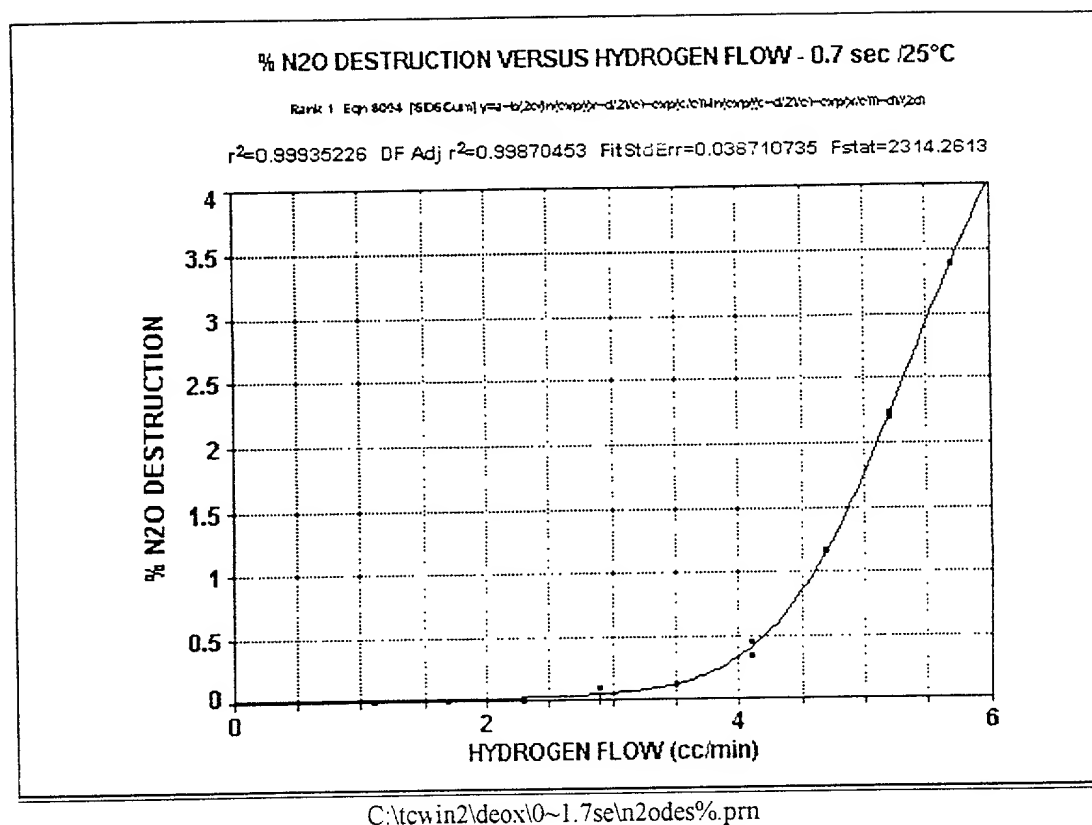


Figure 6

